

THERMOGRAVIMETRIC STUDY OF NOVEL SORBENTS FOR FLUE GAS CLEANUP*

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Keywords: flue gas cleanup, regenerable sorbents, cerium oxide

INTRODUCTION

Several promising new processes are being developed at the Pittsburgh Energy Technology Center (PETC) to remove the sulfur and nitrogen oxides from the flue gas of coal-fired utility boilers. The Fluidized-Bed Copper Oxide Process developed at PETC is one such new technology for the simultaneous removal of 90% of both SO_2 and NO_x from the flue gas¹. This process involves the absorption of SO_2 by copper oxide on an alumina support in conjunction with sorbent catalyzed reduction of NO_x by ammonia addition. Alternate sorbents to $\text{CuO}/\text{Al}_2\text{O}_3$ are also being considered at PETC for possible improvements in reactivity toward SO_2 , regenerability, attrition resistance, and sorbent costs. A similar process concept based on a $\text{CeO}_2/\text{Al}_2\text{O}_3$ sorbent² has been studied recently at PETC and is the subject of this report.

Cerium oxide is a particularly promising new sorbent because ceria imparts resistance to thermal loss of surface area to alumina³; CeO_2 has potential for the uptake of two moles of sulfur per mole of metal to form $\text{Ce}(\text{SO}_4)_2$; CeO_2 sorbent reacts with SO_2 over a fairly wide range of temperature; and when regenerated under the appropriate conditions, $\text{CeO}_2/\text{Al}_2\text{O}_3$ sorbent produces an off-gas stream that can be used conveniently in a Claus plant for conversion into elemental sulfur². The natural abundance of cerium is slightly higher than copper, and extensive deposits are located in the western United States, as well as in Australia, Brazil, India, and China. Rare earth minerals are mined both as a primary product and as a by-product of the mining of such metals as iron (in China), tin, titanium, and zirconium. Cerium is produced as a by-product of the isolation of other rare earths. The current price of cerium oxide is approximately \$1.50-\$2.00 per pound at 90-95% purity.⁴

The effects of sorbent preparation on the reactivity of $\text{CeO}_2/\text{Al}_2\text{O}_3$ sorbents toward SO_2 and on the regenerability of the sorbents have been examined using a thermogravimetric (TG) technique with simulated flue gas and hydrogen, respectively. Potassium-modified $\text{CeO}_2/\text{Al}_2\text{O}_3$ and composite oxides of Co/Ce and Mn/Ce on alumina have also been investigated. Incorporation of potassium into $\text{CeO}_2/\text{Al}_2\text{O}_3$ has been reported to decrease the CeO_2 crystallite size and improve sorbent performance⁵. Several recent catalysis studies on Co/Ce and Mn/Ce composite oxide systems have described high redox properties^{6,7} and catalytic activity for the $\text{CO} + \text{SO}_2$ reaction⁸ and the $\text{CO} + \text{NO}$ reaction⁹. Both cobalt and manganese oxides have been previously identified as

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promising supported sorbents (on alumina) for SO_2 absorption¹⁰. Manganese oxides have been investigated by several researchers for sulfur removal at a number of different conditions. Investigations of $\text{MnO}_x/\text{Al}_2\text{O}_3$ for flue gas desulfurization have been promising but problems have been identified with low manganese loading and some loss of capacity has been observed on repeated cycles of regeneration^{11,12}.

EXPERIMENTAL

Sorbent samples were prepared by aqueous impregnation of 1/16 inch alumina spheres. Reagent-grade, water-soluble cerium salts that can be decomposed thermally at moderate temperatures were selected for testing. The salts selected were ceric ammonium nitrate, cerous ammonium nitrate, cerous nitrate hexahydrate, and cerous acetate. The alumina spheres were obtained from three commercial catalyst manufacturers. After soaking in excess solution, the sorbent pellets were drained, dried in air overnight at 120°C, and calcined in N_2 at 650°C for 6 hours. Metal loadings on the sorbents were varied by changing the concentration of the impregnation solution and were determined by elemental analysis at Huffman Laboratories, Inc., using atomic absorption techniques. Surface areas were determined by the multipoint BET method using an automated Micromeritics Digisorb 2500 instrument with N_2 as adsorbate. Potassium nitrate was added to the K-modified $\text{CeO}_2/\text{Al}_2\text{O}_3$ sorbents by an incipient wetness technique prior to calcination of the sorbent. Composite oxide sorbents were prepared in the same manner as the Ce-only sorbents by simply combining cobalt or manganese nitrate with the cerium nitrate to form a mixed metal impregnation solution (eg. $\text{Co}(\text{NO}_3)_2 + \text{Ce}(\text{NH}_4)_4(\text{NO}_3)_6$ and $\text{Mn}(\text{NO}_3)_2 + \text{Ce}(\text{NO}_3)_3$).

Reactivity of the various sorbent preparations toward SO_2 was measured in a modified Perkin-Elmer TGS-2 Thermogravimetric Analyzer that has been previously described¹³. For these tests, the sample-shielding tube was refabricated using quartz and a large external furnace was used for temperature control. Simulated flue gas was blended from certified gas mixtures and humidified using a sparger. The calculated typical gas composition was 2800-3000 ppm SO_2 ; 480-500 ppm NO; 2.8-3.0 % O_2 ; 13.7-14.7 % CO_2 ; 4.0, 7.0, or 18 % (vol.) H_2O ; and N_2 as the balance. A sample size of 50 mg of sorbent was selected to just fill the quartz sample pan; this corresponds to about 18-20 pellets. A typical TG test sequence was composed of four steps: 1) the sample was heated to the desired reaction temperature at 10°C/minute in dry N_2 ; 2) after allowing the sample to come to equilibrium at the test relative humidity a "dry" sample weight was obtained and the sample was exposed to humidified simulated flue gas for one hour; 3) the sample was regenerated by reduction in H_2 for 30 minutes followed by reoxidation in air for 10 minutes; and 4) the sample was re-exposed to flue gas for 60 minutes.

From the TG thermal curves, the sorbent capacity was calculated from the weight gain after 60 minutes of exposure to simulated flue gas which was sufficient to completely saturate most of the sorbents. For samples with high metal loadings, although the reaction had not completely stopped after 60 minutes, the rate of reaction had dropped to one percent or less of its initial value. The rate of SO_2 uptake was calculated from the weight gain averaged for the first 10 minutes of absorption. This somewhat long time interval was selected for comparison purposes to minimize the relative

uncertainty in measuring small weight gains. [Note: this estimated rate underestimates the true rate since the TG thermal curves show some deviation from linearity after about 5 to 8 minutes. The conversion of the solid is typically 30+ % after 10 minutes.]

RESULTS AND DISCUSSION

The sorbent capacity for SO_2 uptake as a function of temperature is shown in Figure 1 for several different metal loadings. Since cerium nitrates are thermally unstable above 250°C and hydrated ceric sulfate is completely dehydrated at approximately 350°C ¹⁴, all of the weight gain observed during the TG test has been attributed to sulfate formation. X-ray diffraction results for several of the spent $\text{CeO}_2/\text{Al}_2\text{O}_3$ sorbent samples showed weak lines not present in the fresh sorbent. However, these lines could not be assigned to known cerium sulfate compounds and suggested that the CeO_2 is converted to an amorphous or highly dispersed sulfate on exposure to flue gas. Examination of fresh and spent sorbent by FTIR (Fourier transform infrared spectroscopy) clearly showed the presence of sulfate on the spent sorbents, but specific product compounds could not be identified.

As can be seen in Figure 1, at low metal loadings, the sorbent is essentially saturated at 550°C before 60 minutes of exposure to synthetic flue gas. For sorbents at moderate and high metal loading the capacity continues to increase up to 600°C . However, the TG curves are essentially flat for these sorbents after 60 minutes of exposure even though the sorbent has not reached the calculated, theoretical capacity (complete conversion of CeO_2 to $\text{Ce}(\text{SO}_4)_2$). The rate of SO_2 uptake also decreases steadily below about 600°C as shown in Figure 2. Complete regeneration of these $\text{CeO}_2/\text{Al}_2\text{O}_3$ sorbents occurred in 30 minutes or less in hydrogen at temperatures above 550°C . Figure 3 shows the weight loss after 30 minutes of exposure to H_2 expressed as a percentage of the gain during absorption. Some of the sorbents show weight loss on reduction in excess of 100 %, which is probably due to the partial conversion of CeO_2 to Ce_2O_3 or CeAlO_3 ^{15,16}. Based on these observations of the temperature dependence of absorption and regeneration, a temperature of 600°C was selected to compare the various methods of sorbent preparation.

Comparison of the various $\text{CeO}_2/\text{Al}_2\text{O}_3$ sorbents prepared with differing precursor salts showed little or no difference in sorbent capacity between samples with comparable cerium loadings. A slightly higher rate of SO_2 uptake was observed for sorbents prepared using $\text{Ce}(\text{NH}_4)_4(\text{NO}_3)_6$ as the precursor salt. Although $\text{Ce}(\text{NH}_4)_4(\text{NO}_3)_6$ has been shown to produce a highly porous CeO_2 when decomposed at low temperature¹⁷, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ has been reported to produce CeO_2 of smaller crystallite size when calcined at higher temperature¹⁴. The somewhat higher rate of SO_2 uptake observed for sorbents prepared using $\text{Ce}(\text{NH}_4)_4(\text{NO}_3)_6$ as the precursor salt suggests that the crystallite size of the CeO_2 supported on alumina may not follow the same trends observed for pure, unsupported compounds¹⁴. X-ray diffraction results for several of the $\text{CeO}_2/\text{Al}_2\text{O}_3$ sorbent samples were consistent with highly dispersed CeO_2 , but no estimation of crystallite size was made. It should be pointed out that these differences in rate are small and, when experimental uncertainties are taken into consideration, the differences may not be statistically significant. All of the

precursor salts resulted in sorbents with high BET surface areas, 150 to 200 m²/g. However, no correlation was found between total surface area and sorbent capacity or rate of SO₂ uptake. The sorbent capacity and rate of SO₂ uptake were also found to be unaffected by increasing the water content of the simulated flue gas from 4 % to 18 % or by removing nitric oxide from the gas mixture.

Figure 4 shows the SO₂ to CeO₂ mole ratio (stoichiometry) after 60 minutes of exposure to simulated flue gas for sorbents prepared using various precursor salts on three different aluminas. For metal loading below about 5 %, the observed uptake is greater than the amount required to completely convert all the CeO₂ to Ce(SO₄)₂, indicating some uptake by the alumina support. For sorbents with loadings above about 15 %, the utilization drops to below one mole of SO₂ per mole CeO₂. No difference was observed in the utilization of the CeO₂ on alumina from different suppliers. One of the aluminas did have a lower affinity for cerium uptake, that is, the metal retained on this support was significantly lower at a given impregnation solution concentration than for the other two aluminas. Figure 5 shows that the rate of SO₂ uptake was also lower on sorbents prepared using the third support. Simple grinding in a ball mill showed sorbent prepared on this support to be much less rugged than sorbents prepared on the other two supports and no further testing was done with this alumina. The small differences in the measured rate of SO₂ uptake for sorbents prepared on the same support material have been attributed to differences in sample preparation, i.e., the specific precursor cerium salt used.

As noted above, the CeO₂/Al₂O₃ sorbents undergo weight loss during hydrogen reduction at 600°C of 100+ % of the amount of SO₂ uptake. Since some reduction of Ce(IV) to Ce(III) also occurs, the sorbent samples were reoxidized in air prior to subsequent SO₂ absorption measurements. Following this regeneration procedure, the weight percent of any residual material remaining on the sorbent was recorded. The results of these measurements are summarized in Figure 6. For the CeO₂/Al₂O₃ sorbents, the residual was less than one percent of the total sorbent weight. The sorbent was pale yellow in color after regeneration. Ce₂S₃ is reddish-purple or brown. However, there was not sufficient sample produced in these TG tests for a detailed characterization of the residual material. For the CuO/Al₂O₃ sorbent with a 6-7 % Cu loading, a residual of 3-3.5 percent of the total sorbent weight was measured in the TGA test after a similar regeneration, however, both absorption and regeneration of the CuO/Al₂O₃ sorbent were at 400°C. Following regeneration, the CeO₂ sorbent samples were exposed a second time to simulated flue gas. A small decrease in sorbent capacity was observed, but the rate of SO₂ uptake was the same as that measured for the freshly prepared sorbents as can be seen by comparing Figures 5 and 7. For laboratory prepared samples of the CuO/Al₂O₃ sorbent with a 7 % Cu loading, the rate of SO₂ uptake measured in the TGA using the same gas compositions and reaction times but at 400°C, is 1.7 mg SO₂ per g sorbent per minute.

A series of K-modified CeO₂/Al₂O₃ sorbents was prepared with metal loadings of 4 to 12 % Ce and 0.8 % K to investigate reported⁵ improvements in sorbent performance. The rate of SO₂ absorption measured for each of these sorbents at 600°C was the same as for the Ce-only sorbents. The K-modified sorbents have approximately 10-20 % higher mole ratio of SO₂ absorbed to CeO₂ present at comparable metal loadings than

the Ce-only sorbents. No increase in the residual material remaining on the sorbent after regeneration, as compared to the Ce-only sorbents, was observed for the K-modified $\text{CeO}_2/\text{Al}_2\text{O}_3$ sorbents. Figure 8 compares the capacity of a K-modified $\text{CeO}_2/\text{Al}_2\text{O}_3$ sorbent with a Ce-only sorbent, both with 4 % Ce loading. As pointed out above, at this low metal loading the observed sorbent capacity of $\text{CeO}_2/\text{Al}_2\text{O}_3$ at temperatures above 550 °C corresponds to a sulfur to cerium stoichiometry of greater than 2 to 1. This effect is even more pronounced for the K- $\text{CeO}_2/\text{Al}_2\text{O}_3$ sorbent. At 600°C, the excess corresponds to a 115 % utilization of the CeO_2 on the Ce-only sorbent and a 123 % utilization of the sum of CeO_2 and K_2O on the K- $\text{CeO}_2/\text{Al}_2\text{O}_3$ sorbent. Both types of sorbent show the same temperature dependence of SO_2 capacity and show evidence of a mechanism change below about 300°C.

Composite oxides of Co/Ce and Mn/Ce were prepared on the same alumina support to investigate whether the redox properties of these materials⁶⁻⁹ would improve the SO_2 reactivity or regenerability of the Ce-containing flue gas sorbent. $\text{CeO}_2/\text{MnO}_x/\text{Al}_2\text{O}_3$ sorbents were prepared containing 8 and 13 percent cerium with manganese loadings ranging from 0.3 to 3.7 weight percent (mole fraction of manganese in the composite oxides ranged from 0.07 to 0.43). These sorbents had SO_2 reactivities comparable to the Ce-only sorbents of similar Ce loading and maintained their reactivity after regeneration. (The test was carried out for only one regeneration cycle.) However, a substantial amount of residual material (1 to 4 % of the total sorbent weight) was observed to be left on these sorbents after regeneration. No advantage was found in the $\text{CeO}_2/\text{MnO}_x/\text{Al}_2\text{O}_3$ sorbents as compared to the Ce-only sorbent. $\text{CeO}_2/\text{CoO}_x/\text{Al}_2\text{O}_3$ sorbents were prepared containing 5, 10, and 14 percent cerium with cobalt loadings ranging from 0.2 to 2.0 percent (mole fraction of cobalt in the composite oxides ranged from 0.06 to 0.39). Reactivity measurements on these sorbents showed them to be essentially the same as the Ce-only sorbents. In this case no difference in residual material after regeneration in H_2 was observed. The temperature dependence of the SO_2 absorption by the $\text{CeO}_2/\text{CoO}_x/\text{Al}_2\text{O}_3$ sorbent was also examined and found to be essentially the same as for the Ce-only sorbents.

A comparison of the SO_2 reactivity measurements for all four types of sorbents is shown in Figures 9 and 10. The K-modified $\text{CeO}_2/\text{Al}_2\text{O}_3$ and $\text{CeO}_2/\text{Al}_2\text{O}_3$ prepared from $\text{Ce}(\text{NH}_4)_4(\text{NO}_3)_6$ have slightly higher rates of absorption (Figure 9) but the differences are small. The K-modified $\text{CeO}_2/\text{Al}_2\text{O}_3$ sorbents have somewhat higher capacities (Figure 10), but once again the improvement is modest. For laboratory prepared samples of the $\text{CuO}/\text{Al}_2\text{O}_3$ sorbent with a 7 % Cu loading, the rate of SO_2 uptake measured in the TGA using the same gas compositions and reaction times but at 400°C is 1.7 mg SO_2 per g sorbent per minute and the sorbent capacity is 59 mg SO_2 per g sorbent.

CONCLUSIONS

$\text{CeO}_2/\text{Al}_2\text{O}_3$ sorbents have been prepared that have SO_2 reactivity comparable to or slightly higher than the $\text{CuO}/\text{Al}_2\text{O}_3$ sorbent, and can be regenerated in hydrogen with essentially complete removal of sulfur. Residual material remaining on the $\text{CeO}_2/\text{Al}_2\text{O}_3$ sorbents was about one fifth the amount typically seen for the $\text{CuO}/\text{Al}_2\text{O}_3$ sorbent with similar metal loading under similar experimental conditions (TG testing was performed using the same gas compositions and reaction times for both types of sorbents).

However, the temperature of operation is higher for the CeO_2 , 600°C compared to 400°C for CuO . $\text{CeO}_2/\text{MnO}_x/\text{Al}_2\text{O}_3$ and $\text{CeO}_2/\text{CoO}_x/\text{Al}_2\text{O}_3$ sorbents were also prepared that gave quite comparable SO_2 reactivity to the Ce-only sorbent. However, these composite oxide sorbents do not appear to offer an advantage to the Ce-only sorbent when H_2 is the reducing gas. K-modified $\text{CeO}_2/\text{Al}_2\text{O}_3$ sorbents exhibited approximately 10-20 % higher absorption capacity at comparable metal loadings than did the Ce-only sorbents, but the rate of SO_2 uptake was essentially the same.

ACKNOWLEDGEMENTS

The authors would like to thank Dr. S.S. Pollack for providing the X-ray diffraction analysis and Michael Hilterman, Michael Ferrer, and Frank McCown for assistance in obtaining the TG data.

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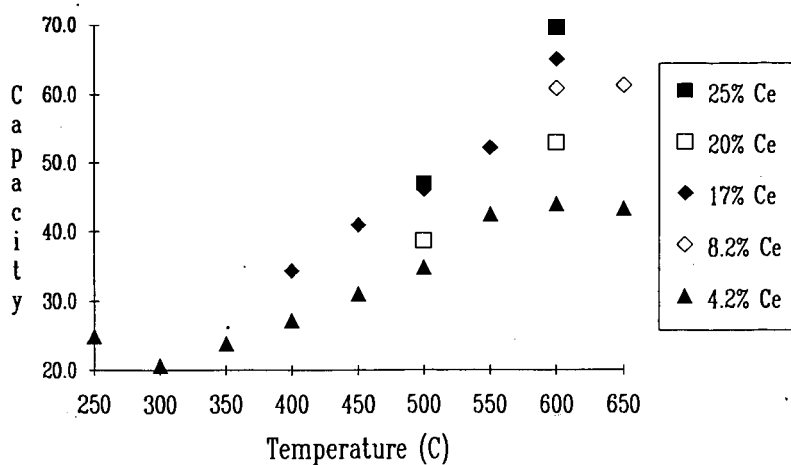


Figure 1. Capacity of $\text{CeO}_2/\text{Al}_2\text{O}_3$ sorbents expressed in mg SO_2 per g sorbent as a function of temperature.

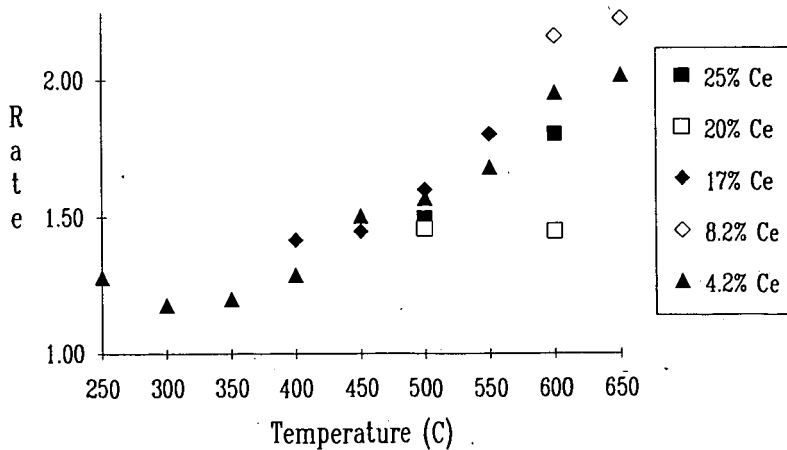


Figure 2. Rate of SO_2 uptake by $\text{CeO}_2/\text{Al}_2\text{O}_3$ sorbents expressed in mg SO_2 per g sorbent per minute as a function of temperature. See text for discussion.

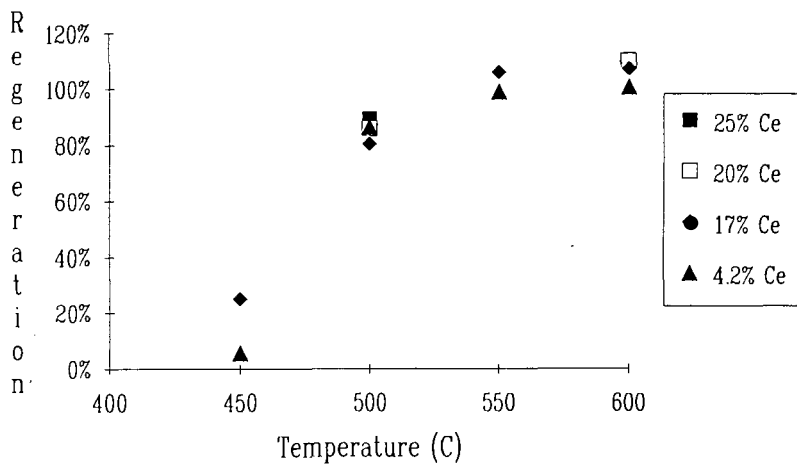


Figure 3. Reduction of spent $\text{CeO}_2/\text{Al}_2\text{O}_3$ sorbents in hydrogen expressed as a percentage of the weight gain observed during SO_2 absorption as a function of temperature.

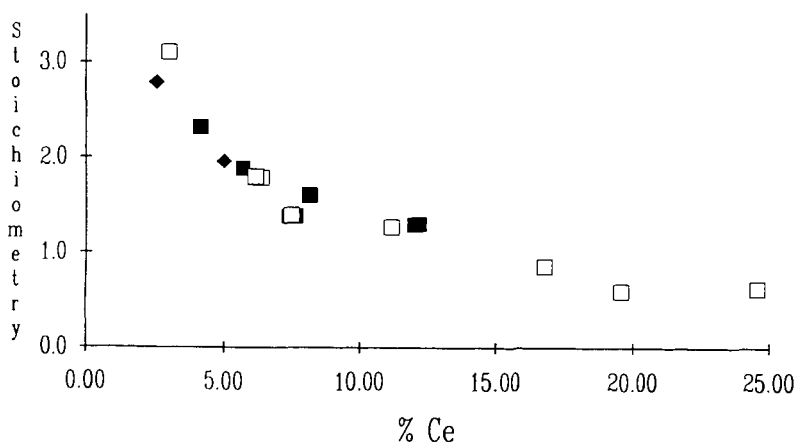


Figure 4. Mole ratio of SO_2 absorbed at saturation at 600°C to CeO_2 on the sorbent as a function of metal loading. Different point symbols represent aluminas from different commercial suppliers.

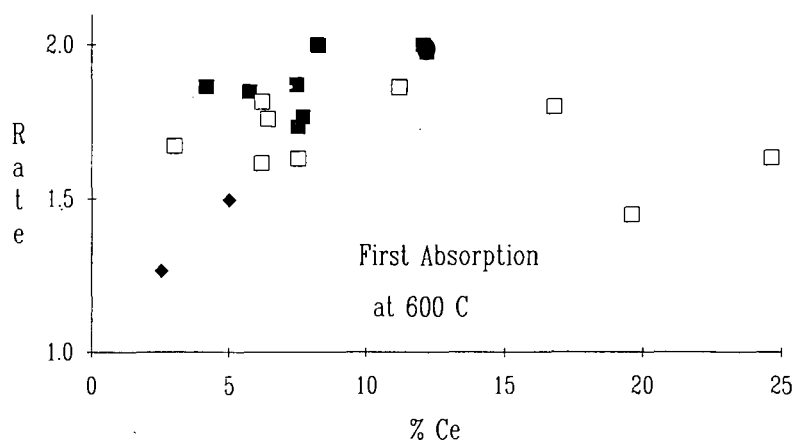


Figure 5. Rate of SO_2 uptake by $\text{CeO}_2/\text{Al}_2\text{O}_3$ sorbents expressed in mg SO_2 per g sorbent per minute as a function of Ce loading. The standard deviation of the rates determined was 0.1 or less. Different point symbols represent aluminas from different commercial suppliers. See text for discussion.

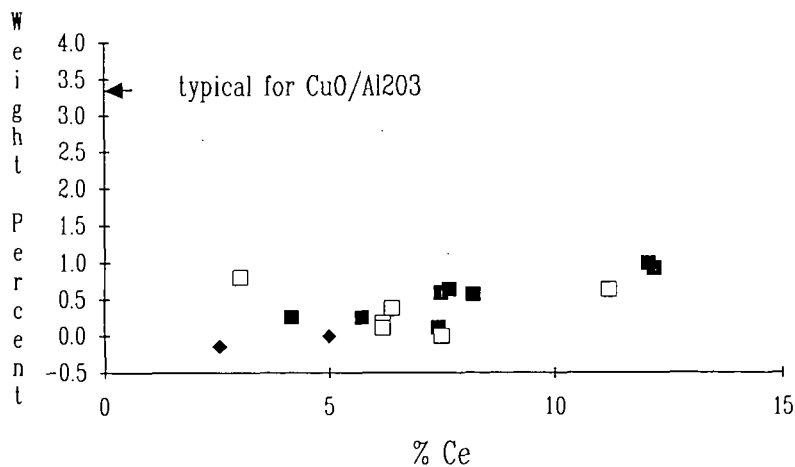


Figure 6. Residual remaining on $\text{CeO}_2/\text{Al}_2\text{O}_3$ sorbents after regeneration in H_2 in the TGA test unit. The value observed for $\text{CuO}/\text{Al}_2\text{O}_3$ under similar conditions is shown for comparison.

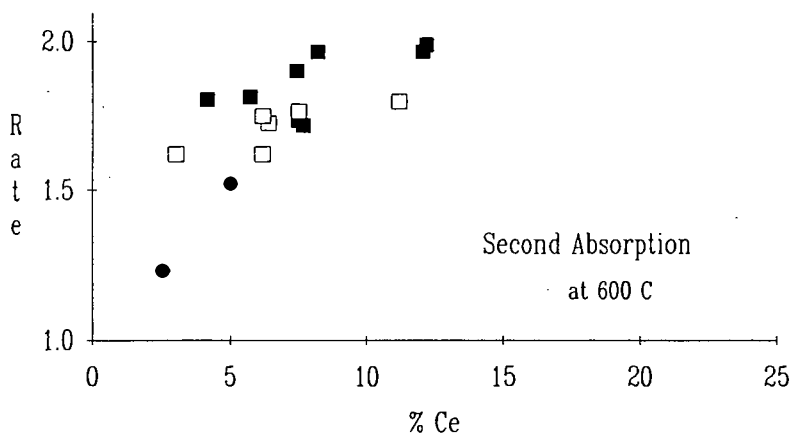


Figure 7. Rate of SO_2 uptake by $\text{CeO}_2/\text{Al}_2\text{O}_3$ sorbents during a second exposure to simulated flue gas after regeneration in H_2 expressed in mg SO_2 per g sorbent per minute as a function of Ce loading. The standard deviation of the rates determined was 0.1 or less. Point shapes represent aluminas from different commercial suppliers. See text for discussion.

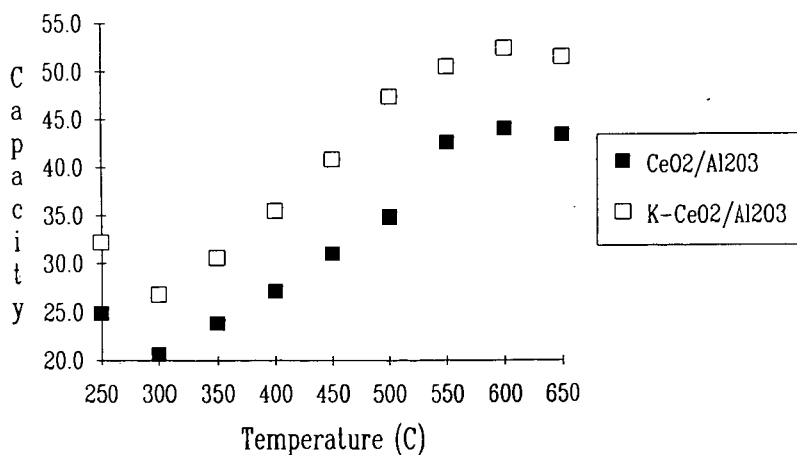


Figure 8. Comparison of SO_2 capacity as a function of temperature of a K- modified and a Ce-only sorbent, both of which contain 4 % Ce. Capacity is expressed in mg SO_2 per g sorbent.

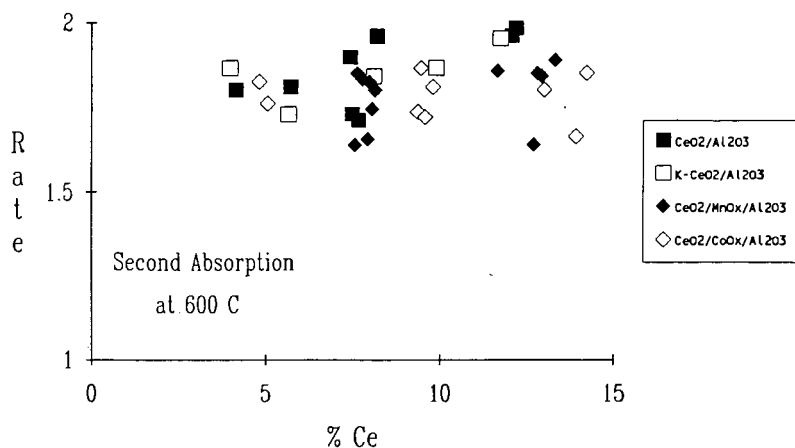


Figure 9. Rate of SO_2 uptake by Ce-containing sorbents during a second exposure to simulated flue gas after regeneration in H_2 expressed in mg SO_2 per g sorbent per minute as a function of Ce loading. The standard deviation of the rates determined was 0.1 or less.

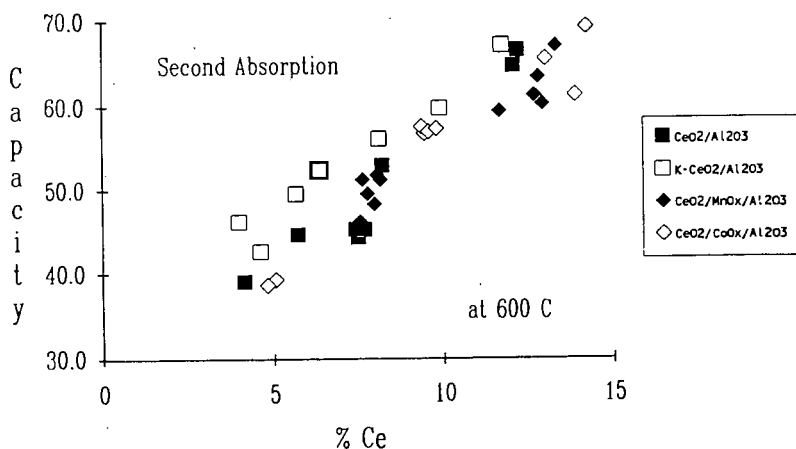


Figure 10. Comparison of SO_2 capacity of Ce-containing sorbents during a second exposure to simulated flue gas after regeneration in H_2 expressed in mg SO_2 per g sorbent as a function of Ce loading. The standard deviation of the capacities determined was 2 or less.